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| FORM-PTO-1390 (Rev. 9-2001) | | U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | ATTORNEY'S DOCKET NUMBER |
| TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371 | | 022701-976 | |
| INTERNATIONAL APPLICATION NO. PCT/FR00/01587 | | INTERNATIONAL FILING DATE 8 June 2000 | U S APPLICATION NO (If known, see 37 C F R 1 5) 10/009732 Unassigned |
| TITLE OF INVENTION SELECTIVE SEPARATION OF IRON BY TREATMENT WITH N ION-EXCHANGING RESIN COMPRISING DIPHOSPHONIC ACID GROUPS | | PRIORITY DATE CLAIMED 15 June 1999 | |
| APPLICANT(S) FOR DO/EO/US Patrice GOTTELAND et al. | | | |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: | | | |
| <p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <ul style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <p>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))</p> <ul style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <ul style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> | | | |
| Items 11 to 20 below concern document(s) or information included: | | | |
| <p>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.</p> <p>14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information:</p> | | | |
| Form PCT/IB/308; Form PCT/IPEA/409; Form PCT/IB/306; Form IPEA 416; International Search Report; and 3 Sheets of Drawings. | | | |



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| U.S. APPLICATION NO (If known, see 37 CFR 1.65) Unassigned | INTERNATIONAL APPLICATION NO PCT/FR00/01587 | ATTORNEY'S DOCKET NUMBER 022701-976 |
| 21. <input checked="" type="checkbox"/> The following fees are submitted: | | CALCULATIONS PTO USE ONLY |
| Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,040.00 (960) International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 (970) International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 (958) International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 (956) International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 (962) | | |
| ENTER APPROPRIATE BASIC FEE AMOUNT = | | \$ 890.00 |
| Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). 20 <input type="checkbox"/> 30 <input type="checkbox"/> | | \$ |
| Claims | Number Filed | Number Extra |
| Total Claims | 13 -20 = | X\$18.00 (966) |
| Independent Claims | 3 -3 = | X\$84.00 (964) |
| Multiple dependent claim(s) (if applicable) | | + \$280.00 (968) |
| TOTAL OF ABOVE CALCULATIONS = | | \$ 890.00 |
| Reduction for 1/2 for filing by small entity, if applicable (see below). | | + \$ |
| SUBTOTAL = | | \$ 890.00 |
| Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)). 20 <input type="checkbox"/> 30 <input type="checkbox"/> | | \$ |
| TOTAL NATIONAL FEE = | | \$ |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property + \$ | | |
| TOTAL FEES ENCLOSED = | | \$ 890.00 |
| | | Amount to be refunded: \$ |
| | | charged: \$ |
| a. <input type="checkbox"/> Small entity status is hereby claimed. b. <input checked="" type="checkbox"/> A check in the amount of \$ 890.00 to cover the above fees is enclosed. c. <input type="checkbox"/> Please charge my Deposit Account No. 02-4800 in the amount of \$ to cover the above fees. A duplicate copy of this sheet is enclosed. d. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4800. A duplicate copy of this sheet is enclosed. NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status. | | |
| SEND ALL CORRESPONDENCE TO: | | |
| Teresa Stanek Rea BURNS, DOANE, SWECKER & MATHIS, L.L.P. P.O. Box 1404 Alexandria, Virginia 22313-1404 (703) 836-6620 | | SIGNATURE Teresa Stanek Rea NAME 30,427 REGISTRATION NUMBER |
| | | December 17, 2001 DATE |

531 Rec'd PCT 17 DEC 2001
Patent
Attorney's Docket No. 022701-976

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of)
Patrice GOTTELAND) Group Art Unit: Unassigned
Application No.: Unassigned) Examiner: Unassigned
(Corresponding to PCT/FR00/01587)
Filed: December 17, 2001)
For: SELECTIVE SEPARATION OF)
IRON BY TREATMENT WITH AN)
ION-EXCHANGING RESIN)
COMPRISING DIPHOSPHONIC)
ACID GROUPS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-captioned application as follows:

IN THE CLAIMS:

Kindly amend claims 1-13 as follows:

1. (Amended) Process for the selective separation of iron present in a solution in the presence of other metal ions, optionally comprising vanadium, comprising treating the solution with an ion-exchange resin comprising diphosphonic acid groups.

2. (Amended) Process according to claim 1, wherein the ion-exchange resin comprises sulphonate groups.

3. (Amended) Process according to claim 1, wherein the solution comprising the metal ions is at a pH of less than 3.

4. (Amended) Process according to claim 1, wherein the solution results from a process for the oxidation of organic compounds in the presence of a catalyst.

5. (Amended) Process for the recycling of a catalyst in a reaction for the oxidation of an organic compound in the presence of a catalyst comprising metal elements, comprising treating the solution comprising the catalyst, after separation of at least the compounds resulting from the oxidation, with an ion-exchange resin comprising diphosphonic acid groups, in order to fix the iron present in the said solution, and in recycling said solution, depleted in iron, as catalytic solution for the oxidation reaction.

6. (Amended) Process according to claim 5, wherein the ion-exchange resin comprises sulphonate groups.

7. (Amended) Process according to claim 5, wherein the oxidation reaction is carried out while using, as an oxidizing agent, a compound selected from the group consisting of oxygen, air, peroxides, aqueous hydrogen peroxide solution and nitric acid.

8. (Amended) Process according to claim 5, wherein the oxidation reaction is the reaction for the oxidation of alcohols and/or ketones to carboxylic acids.

9. (Amended) Process for the manufacture of adipic acid by oxidation of cyclohexanol and/or cyclohexanone in the presence of the catalyst based on metal elements, comprising treating the solution resulting from the oxidation comprising the catalyst, after separation of the adipic acid formed, with at least one ion-exchange resin comprising diphosphonic groups, in order to deplete said solution in iron ions, and in reusing said solution, depleted in iron, as a catalyst for the oxidation reaction.

10. (Amended) Process according to claim 9, wherein the oxidation catalyst is based on copper and vanadium.

11. (Amended) Process according to claim 9, wherein the solution comprising the catalyst is a nitric solution from the elution of an ion-exchange resin which makes it possible to separate the metal ions from the carboxylic acid byproducts from the reaction for the oxidation of cyclohexanol and/or cyclohexanone to adipic acid.

12. (Amended) Process according to claim 9, wherein the ion-exchange resin comprising diposphonic acid groups is regenerated with an acidic solution.

13. (Amended) Process according to claim 12, wherein the regeneration of the resin is carried out with a different acid from nitric acid and said regeneration resin is conditioned with a nitric acid solution or by washing with water before a fresh use.

Application No. Unassigned
Attorney's Docket No. 022701-976
Page 4

REMARKS

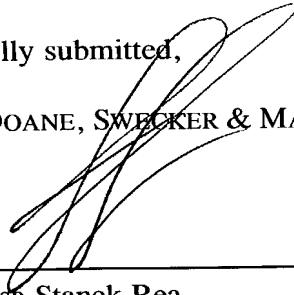
Entry of the foregoing amendments are respectfully requested.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

BURNS, DOANE, SWCKER & MATHIS, L.L.P.

By: _____


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Date: December 17, 2001

Attachment to Preliminary Amendment dated December 17, 2001**Marked-up Claims 1-13**

1. (Amended) Process for the selective separation of iron present in a solution in the presence of other metal ions, [including] optionally comprising vanadium, [characterized in that it consists in] comprising treating the solution with an ion-exchange resin comprising diphosphonic acid groups.

2. (Amended) Process according to claim 1, [characterized in that] wherein the ion-exchange resin comprises sulphonic groups.

3. (Amended) Process according to claim 1 [or 2], [characterized in that] wherein the solution comprising the metal ions is at a pH of less than 3.

4. (Amended) Process according to [one of the preceding claims,] claim 1, [characterized in that] wherein the [abovementioned] solution results from a process for the oxidation of organic compounds in the presence of a catalyst.

5. (Amended) Process for the recycling of a catalyst in a reaction for the oxidation of an organic compound in the presence of a catalyst comprising metal elements, [characterized in that it consists in] comprising treating the solution comprising the catalyst, after separation of at least the compounds resulting from the oxidation, with an ion-exchange resin comprising diphosphonic acid groups, in order to fix the iron present in the

Attachment to Preliminary Amendment dated December 17, 2001

Marked-up Claims 1-13

said solution, and in recycling [the] said solution, depleted in iron, as catalytic solution for the oxidation reaction.

6. (Amended) Process according to claim 5, [characterized in that] wherein the ion-exchange resin comprises sulphonic groups.

7. (Amended) Process according to claim 5 [or 6], [characterized in that] wherein the oxidation reaction is carried out while using, as an oxidizing agent, a compound [chosen] selected from the group consisting of oxygen, air, peroxides, aqueous hydrogen peroxide solution and nitric acid.

8. (Amended) Process according to [one of claims 5 to 7,] claim 5,
[characterized in that] wherein the oxidation reaction is the reaction for the oxidation of
alcohols and/or ketones to carboxylic acids.

9. (Amended) Process for the manufacture of adipic acid by oxidation of cyclohexanol and/or cyclohexanone in the presence of the catalyst based on metal elements, [characterized in that it consists in] comprising treating the solution resulting from the oxidation comprising the catalyst, after separation of the adipic acid formed, with at least one ion-exchange resin comprising diphosphonic groups, in order to deplete [the] said

Attachment to Preliminary Amendment dated December 17, 2001

Marked-up Claims 1-13

solution in iron ions, and in reusing [the] said solution, depleted in iron, as a catalyst for the oxidation reaction.

10. (Amended) Process according to claim 9, [characterized in that] wherein the oxidation catalyst is based on copper and vanadium.

11. (Amended) Process according to claim 9 [or 10], [characterized in that] wherein the solution comprising the catalyst is a nitric solution from the elution of an ion-exchange resin which makes it possible to separate the metal ions from the carboxylic acid byproducts from the reaction for the oxidation of cyclohexanol and/or cyclohexanone to adipic acid.

12. (Amended) Process according to [one of claims 9 to 11] claim 9, [characterized in that] wherein the ion-exchange resin comprising diphosphonic acid groups is regenerated with an acidic solution.

13. (Amended) Process according to claim 12, [characterized in that] wherein the regeneration of the resin is carried out with a different acid from nitric acid and [the] said regeneration resin is conditioned with a nitric acid solution or by washing with water before a fresh use.

PROCESS FOR THE SEPARATION OF IRON FROM OTHER
METAL IONS, AND PROCESS FOR RECYCLING CATALYSTS
IN REACTIONS FOR THE OXIDATION OF ALCOHOLS AND
KETONES TO CARBOXYLIC ACID

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The invention relates to a process for selectively separating iron from other metal ions, in particular ions present in certain oxidation catalysts.

It also relates to a process for recycling catalysts in the reaction for the oxidation of alcohols and optionally ketones to carboxylic acids and more particularly the oxidation of 10 cyclic alcohols and cyclic ketones to dicarboxylic acids, such as the oxidation of cyclohexanol and/or cyclohexanone to adipic acid.

Thus, it is known to manufacture adipic acid by nitric oxidation of a mixture of cyclohexanol and cyclohexanone. This oxidation is generally carried out in the presence of a catalyst comprising vanadium and copper.

15 The solution recovered after separation of the dicarboxylic acids and in particular of adipic acid is treated in order to allow the catalyst to be recycled in the oxidation reaction.

Several processes for the treatment of this solution have been provided. For example, the metals present in the solution can be extracted by treatment with ion-exchange resins. The solution, purified of metals, comprises the byproducts from the synthesis of 20 adipic acid, namely glutaric and succinic acids. Such a process is disclosed, for example, in Patent US 3,965,164.

However, this process does not allow iron ions, originating in particular from the corrosion of the plants, to be removed. Thus, the catalyst is enriched in iron at each recycling cycle. This enriching can decrease the efficiency of the catalyst or can also 25 contaminate the adipic acid manufactured.

Several processes have been provided for at least partially removing the iron without loss of vanadium and of copper.

Other processes consist in selectively and differentially eluting the vanadium and the copper from the ion-exchange resin by using nitric acid solutions at a more or less high concentration or elution solutions comprising acids other than nitric acid or phosphonic acid (SU 690,320, US 3,554,692).

5 However, these processes do not make possible selective removal of the iron without significant loss of vanadium or copper, in view of the ratio of very low concentration of iron with respect to the other two metal ions.

To overcome these disadvantages, European Patent Application No. 0,761,636 provides a process which consists in treating the eluate comprising the iron, copper and 10 vanadium ions with a second ion-exchange resin comprising aminophosphoric groups.

Although improving the prior processes, this process does not make it possible to remove most of the iron ions without loss, in particular, of vanadium ions, which is highly prejudicial to the oxidation process. This is because these resins can have a satisfactory selectivity for iron with respect to the vanadium only under very acidic pH conditions, of 15 markedly less than 1, that is to say when the metal compounds are present in a concentrated nitric acid solution, for example.

One of the aims of the present invention is to provide a novel process which makes it possible to selectively separate the iron from other metal ions, in particular from the vanadium ions, and thus to provide a very efficient process for the recycling of the catalyst 20 for the oxidation of organic compounds, more particularly of alcohols and/or of ketones to carboxylic acids and more preferably still of cyclohexanol and/or cyclohexanone to adipic acid.

To this end, the invention provides a process for selectively separating the iron present in a solution in the presence of other metal ions, including vanadium. These 25 solutions are generally solutions originating from processes for the oxidation of an organic compound in the presence of a vanadium-based catalyst.

According to the characteristic of the invention, the solution comprising the said metal ions is treated with an ion-exchange resin comprising diphosphonic acid groups.

During this treatment, the iron is fixed by the resin; the metal ions, such as, in particular, copper and vanadium, remain in the treated solution.

5 The process of the invention makes it possible to fix to the resin at least 80% of the iron present in the solution.

According to another characteristic of the invention, the solution to be treated comprising the metal ions has a very low pH, advantageously of less than 3 and of preferably less than 2.

10 According to a preferred characteristic of the invention, the ion-exchange resin also comprises sulphonic groups.

The use of resins comprising diphosphonic acid groups and optionally sulphonic groups makes it possible, in a noteworthy way, to fix the iron present in a solution without fixing other metal cations, such as copper and more particularly vanadium.

15 This process applies more particularly to the recycling of the catalysts in reactions for the oxidation of organic compounds and more particularly of alcohols and/or ketones to carboxylic acids. Such an oxidation process also constitutes a subject-matter of the present invention.

This is because, in these processes, the iron is often a contaminating element 20 originating mainly from corrosive attack on the equipment by the oxidation medium.

Mention may be made, as oxidation reactions in which the process of the invention makes possible efficient recycling of the catalyst, of oxidation reactions using, as oxidizing agent, a compound chosen from the group consisting of oxygen, air, peroxides, aqueous hydrogen peroxide solution and nitric acid.

25 Mention may be made, as example of oxidation reaction, of the reaction for the deperoxidation of cyclohexane hydroperoxide.

It applies in particular in the process for the manufacture of adipic acid from the oxidation of cyclohexanol and/or cyclohexanone, which process is also a subject-matter of the present invention.

In such processes, it is important from an economic viewpoint, and to avoid 5 discharge of metals to the environment, to recycle the catalyst comprising metal elements, such as, for example, copper and/or vanadium, while minimizing the bleeds or the flow of unrecycled catalyst.

However, in order for such a recycling process not to disturb the oxidation reaction, it is necessary to avoid the recycling or the concentration of certain products or byproducts 10 which have a poisoning effect on the catalyst or which can contaminate the products manufactured.

In the case of the manufacture of adipic acid by oxidation of cyclohexanol and/or cyclohexanone with an oxidant such as nitric acid, corrosion of the plants results in particular in the presence of iron in the reaction mixture.

15 It is consequently important for the functioning of the process to provide for the removal of the iron. This removal must be obtained without removal of the other metal ions used as catalyst for the oxidation, such as copper and vanadium.

The process of the invention makes it possible to carry out this removal of the iron by treatment of the solution comprising the various metal ions recovered after separation of the 20 organic compounds and in particular of the carboxylic acid or acids formed.

This removal of the iron is obtained by treatment of the said solution with an ion-exchange resin comprising diphosphonic acid groups and optionally sulphonic groups.

After treatment, the solution comprises the metal ions with the exception of iron ions, the latter being fixed to the resin. The amount fixed is advantageously greater than 80% of 25 the amount initially present in the solution.

Thus, the process of the invention makes it possible to recycle a solution comprising the metal ions of use in the catalysis with a minimum loss of the said ions and an absence of the iron ions or a presence of the latter at a very low and untroublesome concentration.

Thus, in the case of the manufacture of adipic acid by oxidation of an alcohol and/or

5 a ketone by nitric acid, the treatment of the aqueous solution comprising the metal ions originating from the oxidation catalyst, namely, preferentially, vanadium and copper, with an ion-exchange resin comprising diphosphonic groups and optionally sulphonic groups makes it possible to remove the iron originating in particular from the corrosion of the plants and to recycle a catalytic solution with a minimum loss of catalytic elements, in particular of

10 vanadium and of copper.

In addition, as the concentration of iron in the reaction mixture is maintained at a very low level, the process of the invention makes possible production of adipic acid with a very low, indeed even zero, content of iron.

The treatment of the solution is carried out, in a first embodiment, after extraction of

15 the adipic acid and optionally separation of the precipitated vanadium.

The solution, purified of iron, can subsequently be treated with a second ion-exchange resin which fixes all the metal ions, in order to avoid recycling a solution comprising organic byproducts from the oxidation reaction, such as glutaric acid and/or succinic acid. The recycled catalytic solution is composed of the solution from the elution of

20 the said resin, which solution is generally composed of a nitric acid solution.

In a second embodiment, the treatment on an ion-exchange resin comprising diphosphonic acid groups and optionally comprising sulphonic groups can be carried out on the solution from the elution of the resin which makes it possible to separate the organic byproducts from the metal ions which are described above.

25 According to another characteristic of the invention, the ion-exchange resin comprising diphosphonic groups and optionally comprising sulphonic groups is regenerated

by elution with an inorganic acid solution. Mention may be made, as suitable inorganic acids, of nitric acid, phosphoric acid or sulphuric acid.

Preferably, it is preferable to use an acid identical to that used to prepare the catalytic oxidation solution, generally nitric acid, in order thus to avoid contamination of the reaction mixture by another acid.

However, it is possible to regenerate the resin with a different acid and then to condition the resin with the acid identical to that of the catalytic solution, for example nitric acid, before a fresh use. It is also possible to carry out this conditioning by washing the resin with water several times in order to remove the traces of elution acid.

10 The conditions for carrying out the treatment on an ion-exchange resin in accordance with the invention are the conventional conditions for the use of resins. Thus, the temperature for carrying out this treatment can vary from room temperature (approximately 20°C) to a temperature of approximately 100°C, preferably between 30°C and 80°C.

Likewise, the concentration of the acidic regeneration solution is conventional. It can, for example, be between 10% and 40% by weight.

The ion-exchange resins in accordance with the invention comprising diposphonic acid groups and optionally sulphonic groups are, for example, those disclosed in Patents US 5,449,462 and 5,281,631.

These resins are obtained by polymerization of various monomers, some of which comprise diphosphonic acid groups. The resin can be a polystyrene resin with diphosphonic groups.

The resin can also comprise carboxylic groups and/or sulphonate groups.

The processes for the manufacture of these resins are disclosed in the two abovementioned United States patents. The description of their structures is also given in these documents.

These resins are sold in particular by the company Eichrom Industries under the trademark Eichrom Diphonix®.

Other advantages and details of the invention will become apparent in the light of the examples given hereinbelow solely by way of indication.

EXAMPLE 1

600 ml of an aqueous solution comprising 1.3% of nitric acid, 10,485 ppm of copper ion, 1353 ppm of iron ion and 281 ppm of vanadium ion are introduced into a receptacle.

50 ml of ion-exchange resin sold under the name Eichrom Diphonix® are added.

The mixture is stirred for variable times.

The concentration of metals in the solution is measured after being brought into contact for variable periods of time.

10 The percentage of metal fixed to the resin as a function of the duration of treatment is represented in graph 1.

It is easily observed from this graph that the iron is virtually completely fixed to the resin. In contrast, small amounts of vanadium and of copper are fixed at the beginning of the operation, these amounts remaining constant throughout the operation.

15 The treatment thus makes possible selective separation of the iron from the other metal ions and in particular from the vanadium.

COMPARATIVE EXAMPLES 2 AND 3

Similar tests were carried out with ion-exchange resins comprising aminophosphonic groups in accordance with European Patent 0,761,636.

20 The two resins used are respectively a resin sold under the name Purolite S-940 and
a resin sold by the company Röhm & Haas under the tradename C467.

The percentage of metal ions fixed as a function of the duration of treatment is represented in graphs 2 and 3 for the resin S940 and C467 respectively.

As may be observed, these resins fix at most 60% of the iron present in the solution
25 but, above all, fix virtually all the vanadium.

Consequently, these resins, used in processes for recycling vanadium-based oxidation catalysts, have a major disadvantage.

In addition, they do not make it possible to carry out the selective separation of the iron with respect to the vanadium.

EXAMPLES 4, 5c AND 6c

Example 1 is repeated on a solution comprising 19.9% of nitric acid, 8875 ppm of 5 copper, 1192 ppm of iron and 165 ppm of vanadium.

This solution corresponds to the solution of eluates with nitric acid of a cation-exchange resin on which has been treated a solution originating from a process for the oxidation of cyclohexanol with nitric acid.

The results obtained with an Eichrom Diphonix® resin, the Purolite S-940 resin and 10 the Röhm & Haas C467 resin are represented respectively by the graphs 4, 5 and 6.

As in the preceding examples, the resin in accordance with the invention makes it possible to fix a large amount of iron (at least 60% of the starting amount) while fixing a minimum of the other vanadium and copper cations.

In contrast, the other two resins fix a significant amount of vanadium simultaneously 15 with the iron.

EXAMPLE 7 - Regeneration of the Eichrom Diphonix® resin

The resins, laden with iron, obtained in Examples 1 and 4 are regenerated by elution with various acidic solutions by passing 100 ml of elution solution through 10 ml of resin.

The results obtained are collated in the following table. These results represent the 20 percentage of metal ions which are recovered by the elution with respect to the amount fixed.

| | Resin, Example 1 | | | Resin, Example 4 | | |
|--------------------------------|------------------|----|----|------------------|----|----|
| | Cu | Fe | V | Cu | Fe | V |
| HNO ₃ | 95 | 29 | 97 | 52 | 14 | 56 |
| H ₂ SO ₄ | 91 | 35 | 95 | 50 | 21 | 53 |
| H ₃ PO ₄ | 87 | 50 | 90 | 45 | 37 | 50 |

CLAIMS

1. Process for the selective separation of iron present in a solution in the presence of other metal ions, including vanadium, characterized in that it consists in treating the solution with an ion-exchange resin comprising diphosphonic acid groups.
- 5 2. Process according to claim 1, characterized in that the ion-exchange resin comprises sulphonic groups.
3. Process according to claim 1 or 2, characterized in that the solution comprising the metal ions is at a pH of less than 3.
4. Process according to one of the preceding claims, characterized in that the 10 abovementioned solution results from a process for the oxidation of organic compounds in the presence of a catalyst.
5. Process for the recycling of a catalyst in a reaction for the oxidation of an organic compound in the presence of a catalyst comprising metal elements, characterized in that it consists in treating the solution comprising the catalyst, after separation of at least the 15 compounds resulting from the oxidation, with an ion-exchange resin comprising diphosphonic acid groups, in order to fix the iron present in the said solution, and in recycling the said solution, depleted in iron, as catalytic solution for the oxidation reaction.
6. Process according to claim 5, characterized in that the ion-exchange resin comprises sulphonic groups.
- 20 7. Process according to claim 5 or 6, characterized in that the oxidation reaction is carried out while using, as oxidizing agent, a compound chosen from the group consisting of oxygen, air, peroxides, aqueous hydrogen peroxide solution and nitric acid.
8. Process according to one of claims 5 to 7, characterized in that the oxidation reaction is the reaction for the oxidation of alcohols and/or ketones to carboxylic acids.
- 25 9. Process for the manufacture of adipic acid by oxidation of cyclohexanol and/or cyclohexanone in the presence of a catalyst based on metal elements, characterized in that it consists in treating the solution resulting from the oxidation comprising the catalyst, after

separation of the adipic acid formed, with at least one ion-exchange resin comprising diphosphonic groups, in order to deplete the said solution in iron ions, and in reusing the said solution, depleted in iron, as catalyst for the oxidation reaction.

10. Process according to claim 9, characterized in that the oxidation catalyst is based on 5 copper and vanadium.

11. Process according to claim 9 or 10, characterized in that the solution comprising the catalyst is a nitric solution from the elution of an ion-exchange resin which makes it possible to separate the metal ions from the carboxylic acid byproducts from the reaction for the oxidation of cyclohexanol and/or cyclohexanone to adipic acid.

10 12. Process according to one of claims 9 to 11, characterized in that the ion-exchange resin comprising diphosphonic acid groups is regenerated with an acidic solution.

13. Process according to claim 12, characterized in that the regeneration of the resin is carried out with a different acid from nitric acid and the said regenerated resin is conditioned with a nitric acid solution or by washing with water before a fresh use.

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(54) Title: SELECTIVE SEPARATION OF IRON BY TREATMENT WITH AN ION-EXCHANGING RESIN COMPRISING
DIPHOSPHONIC ACID GROUPS

(54) Titre: SEPARATION SELECTIVE DU FER PAR TRAITEMENT AVEC UNE RESINE ECHANGEUSE D'IONS COMPRE-
NANT DES GROUPEMENTS ACIDES DIPHOSPHONIQUES

A1
WO 00/76661
(57) Abstract: The invention concerns a method for the selective separation of iron from other metal ions in particular ions present in certain oxidation catalysts. The invention also concerns a method for recycling oxidation catalysts in the oxidation reaction of alcohols and/or ketones into carboxylic acids and more particularly the oxidation of cyclic alcohols and/or cyclic ketones into dicarboxylic acids such as oxidation of cyclohexanol and/or cyclohexanone into adipic acid. Said method consists in treating the solution containing the oxidation catalyst, before recycling it, with an ion exchanging resin for selectively separating the iron from other metal elements in particular copper and vanadium, the ion exchanging resin comprising diphosphonic acid groups (for example, Diphonix)

(57) Abrégé: L'invention concerne un procédé pour séparer sélectivement le fer d'autres ions métalliques notamment des ions présents dans certains catalyseurs d'oxydation. Elle se rapporte également à un procédé de recyclage des catalyseurs dans la réaction d'oxydation d'alcools et/ou cétones en acides carboxyliques et plus particulièrement l'oxydation d'alcools cycliques et/ou cétones cycliques en acides dicarboxyliques tels que l'oxydation du cyclohexanol et/ou cyclohexanone en acide adipique. Ce procédé consiste à traiter la solution contenant le catalyseur d'oxydation, avant son recyclage, par une résine échangeuse d'ions permettant de séparer sélectivement le fer des autres éléments métalliques notamment du cuivre et du vanadium. La résine échangeuse d'ions comprenant des groupements acides diphosphoniques (e.g. Diphonix).

**PROCESS FOR THE SEPARATION OF IRON FROM OTHER
METAL IONS, AND PROCESS FOR RECYCLING CATALYSTS
IN REACTIONS FOR THE OXIDATION OF ALCOHOLS AND
KETONES TO CARBOXYLIC ACID**

The invention relates to a process for selectively separating iron from other metal ions, in particular ions present in certain oxidation catalysts.

It also relates to a process for recycling catalysts in the reaction for the oxidation of alcohols and/or ketones to carboxylic acids and more particularly the oxidation of cyclic alcohols and/or cyclic ketones to dicarboxylic acids, such as the oxidation of cyclohexanol and/or cyclohexanone to adipic acid. This process consists in treating the solution comprising the oxidation catalyst, before it is recycled, with an ion-exchange resin which makes it possible to selectively separate the iron from the other metal elements, in particular from copper and from vanadium.

022701-976
Attorney's Docket No.

**COMBINED DECLARATION AND POWER OF ATTORNEY
FOR UTILITY OR DESIGN PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**SELECTIVE SEPARATION OF IRON BY TREATMENT WITH AN ION-EXCHANGING RESIN
COMPRISING DIPHOSPHONIC ACID GROUPS**

the specification of which (check only one item below):

is attached hereto.

was filed as United States application
Number _____ on _____
and was amended on _____ (if applicable).

was filed as PCT international application
Number PCT/FR00/01587 on JUNE 8, 2000
and was amended on DECEMBER 17 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §§119 (a)-(d), 172 or 365 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

| PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §§119(a)-(d), 172 or 365: | | | |
|--|--------------------|--------------------------------------|---|
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| | | | <input type="checkbox"/> Yes <input type="checkbox"/> No |
| | | | <input type="checkbox"/> Yes <input type="checkbox"/> No |

Combined Declaration and Power of Attorney
for Utility or Design Patent Application
Attorney's Docket No. 022701-976
Page 2 of 2

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

| | | | |
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